FEDERAL REPUBLIC OF GERMANY

GERMAN PATENT OFFICE

Patent Disclosure 25 16 097

File Number P 25 16 097.8

Date of Submission 4/12/75

Date of Disclosure 11/6/75

Union priority: 4/19/74 Great Britain 17371-74

Designation: Paper filler

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(Prio: April 19, 1974
GB 17371/74 - 12184)

Hamburg, April 10, 1975

Paper Filler

The invention deals with the production of paper or similar fiber-containing web materials. With the invention, a composition is proposed which serves as a replacement for fibers in this type of materials; that is, a filler composition or an extender, as well as a process for the production of a fiber-containing web material with a filler composition, and finally, a paper-type material which contains a specified filler.

In the production of paper it is customary to add to the fiber web a specified quantity of finely divided inorganic filler; by this means, a saving of expensive cellulose or other fibers is achieved and opacity, color, and surface properties are improved. One filler extensively used is clay; chalk or calcium carbonate is also employed. The quantity of filler permissible in paper production is limited by the fact that fillers impair the strength of the paper.

The objective of the invention is to develop a paper filler composition which, even when employed in considerable quantities, leads to no significant loss of strength, as normally occurs with smaller quantities of known fillers.

It was then found that the tendency of filler particles to weaken the bonds between the fibers decreases when one combines a fine-particled, cationic, inorganic material like calcium carbonate with a synthetic polymeric resin, so that the resin particles adhere to the surface of the filler particles. It was further discovered that for this purpose the synthetic polymeric resin could be anionic. The inorganic filler particles can be cationic as supplied, or they can be made cationic by appropriate treatment. The cationic treatment of inorganic fillers is known; for example, calcium carbonate can be mixed with a small quantity of cationic starch, in order to give it a positive zeta potential.

Preferably, the anionic properties of the synthetic polymeric resin and the cationic properties of the inorganic filler are equal, so that the filler composition has a zeta potential of practically 0.

The object of the present invention is a composition for the replacement of fibers in a paper-type web material on the basis of a fine-particled inorganic filler like calcium carbonate, which is so characterized that the filler occurs in the form of particles which display a cationic potential as supplied, or are made cationic, and the filler is combined with an anionic polymeric resin.

The composition is supplied preferably in the form of an aqueous dispersion.

The preferred inorganic filler is calcium carbonate, which is advantageously milled so that the particle size is less than about 30 millimicrons. Other suitable inorganic fillers for the invention composition are calcium silicate, talc, clay, diatomaceous earth, calcium sulfate, silicic acid, as well as a mixture of calcium sulfate and calcium phosphate (known in the trade as "Syloid White"), or mixtures of these fillers.

A cationic calcium carbonate which can find use in the composition is sold in Italy by the Silca company under the trade name MICROCEL. It has the particle size distribution shown in the attached figure (according to the Coulter counter method).

The resin is a synthetic polymer, which is preferably supplied in the form of an aqueous latex. Upon drying of the latex at room temperature, the preferred resins are not film-forming, or they lead to an inelastic film, that is, a film with a stretch limit or break elongation of less than 200% and preferably less than 20%. The preferred polymer is a styrene/butadiene copolymer with a styrene content of at least 60% by weight. An especially preferred polymer is sold under the trade name POL-X-1110.

Other suitable anionic synthetic resins for the invention composition are anionic latices of polyvinyl acetate or of acrylic copolymers. It has already been proposed to combine a fine-particled inorganic filler like calcium carbonate with a polymer prepared from an acrylic monomer, in order to produce a paper filler (GB-PS 1 353 015), however the polymer must be combined with a coagulating agent like borax or alum, in order to produce

a gel which surrounds the particles and leads to the agglomeration of the inorganic filler. This is completely contrary to the concept of the present invention, which is that the cationic filler is surrounded by an anionic resin layer through approximate equalization of the ionic properties, so that as far as possible, an agglomeration is avoided. In the composition according to the invention, the resin forms a firmly adhering coating on the filler particles, which is not removed by screening, purification, or cleaning.

The composition can be obtained by mixing an aqueous latex of the resin with an aqueous suspension of the cationic inorganic filler particles. The latex is best added in a quantity of 1 to 20 parts by weight of resin on 100 parts by weight of filler in the suspension (based upon dry weight). The filler composition thus obtained can replace 5 to 50% of the cellulose fibers.

The filler composition according to the invention can be added to the pulp during paper production in the hollander, pulper, refiner, or to another stage of the preparation. The filler mixture in the form of a liquid suspension can be added to the pulp after the acid sizing agent, for example, a rosin/alum-sizing agent.

The pulp containing the filler mixture is then processed into a material in web form by means of customary paper manufacturing methods, that is, the pulp is converted into moist webs, and dried after dewatering. The filler quantity in the pulp can be sufficient to attain a content of up to 50% by weight; for example, 20 to 50% by weight of calcium carbonate or another filler, based upon the total weight of solid materials.

A pulp containing the filler mixture is especially suitable as the top layer (liner ply) of a multi-ply paperboard. For this purpose the basis weight of the filled liner ply is advantageously about 10 to 12 g/m^2. Through its employment as the outer layer, the filler leads to the desired opacity, good surface structure and shape stability without loss of strength. With the invention, furthermore, a paper-type fiber web material is proposed, for example, a paper or paperboard, with a content of inorganic filler which is so characterized that the filler particles adhere through ionic adhesion forces to particles of a polymeric resin.

A surface active agent or retention aid can likewise be present in the invention composition. Surface active agents or emulsifying agents already contained in the latex should of course be compatible with the cationic filler.

The equalization between the anionic and the cationic potential in the invention composition insures that the cationic inorganic filler particles do not agglomerate or coagulate when the anionic latex is mixed with the filler suspension.

For illustration of the invention and its advantages the following examples will serve. The calcium carbonate employed in these examples consists of 0.6% cationic starch and 99% $CaCO_3$

Example 1

A typical paper produced according to the invention has the following composition:

Cellulose fibers	50 parts
Calcium carbonate	up to 48 parts
Polymer	1 to 10 parts

A high proportion of this filler can be present in the paper without noticeably impairing its mechanical properties. The paper shows an improvement with respect to smoothness, uniformity, stability, opacity, and printability.

In a comparison experiment with the filler according to the present invention paper was produced with 8 to 10% of a customary filler based upon clay, in which this filled paper produced in the usual manner had a breaking length of 6500 m. For the investigation of the filler according to the invention, the 8 to 10% of clay was replaced by 22% of the filler mixture according to the invention, and the quantity of cellulose pulp at the same time was correspondingly decreased. The paper production then proceeded as before, and the breaking length of the paper containing the filler according to the invention was only slightly below that of the paper with a content of 8 to 10% of clay, namely, 5600 m. For comparison it s ould be added that the in-

crease of the clay content of the paper from 8 to 10% to the higher value of 22% leads to a decrease of the breaking length to about 1000 m.

Example 2

35 parts of a styrene/butadiene copolymer bonding agent with a solids content of 8 parts (corresponding to 2% of polymeric bonding agent based upon the calcium carbonate) were added to 1000 parts of an aqueous suspension containing 40% of cationic, starch-treated calcium carbonate. The filler composition was added to a cellulose pulp which contained 1400 parts of cellulose (based upon dry weight), which had been beaten to a freeness of 40° S.R. After several minutes of mixing with the paper pulp, paper was produced with the aid of customary apparatus.

The following results were obtained, in comparison with a customary paper loaded with 9% of clay:

	With clay as filler	With filler according to the invention
Basis wt. in g/m^2	60	58
Breaking length (length which can be supported without breaking) in m	4200	4600
Elongation at rupture in %	3.7	4.4
Theoretical ash content in %	12	22.2
Ash content in %	9	18
Brightness	80	83
Opacity	75	77

Example 3

89 parts of a styrene/butadiene-copolymer bonding agent with a solids content of 20 parts (corresponding to 5% of polymeric bonding agent based upon the calcium carbonate) were added to 1000 parts of an aqueous suspension containing 40% of cationic calcium carbonate. The filler composition was added to 700 parts by weight (dry basis) of a cellulose pulp as described in example 2.

The following results were obtained, in comparison with a customary paper loaded with 9% of clay:

	With clay as filler	With filler according to the invention
Basis weight in g/m^2	60	60
Breaking length in m	4200	3550
Elongation at rupture in %	3.7	3.2
Thecretical ash content in %	12	36.4
Ash content in %	9	33.3
Brightness	80	84
Opacity	73	83

Example 4

A filler composition was produced as described in Example 3, that is, the quantity of polymeric bonding agent, based upon cationic calcium carbonate, was 5%:

20 parts by weight (dry basis) of the filler composition was added to a pulp which contained 40 parts by weight (dry basis) of dewatered sulfite pulp and 40 parts by weight (dry basis) of bleached waste paper, which had been beaten to a freeness of 65° S. R.

In comparison with a customary paper containing 6% of clay as filler, the following results were obtained:

	With clay as filler	With filler according to the invention
Basis weight in g/m^2	50	50
Breaking length in m	4000	3800
Elongation at rupture in %	2.4	2.7
Ash content in %	6.0	16.0

Example 5

71 parts of a styrene/butadiene copolymer latex with a solids content of 16 parts, which corresponded to 4% of polymeric bonding agent based upon the calcium carbonate, were added to 1000 parts of an aqueous suspension containing 40% of cationic calcium carbonate. The filler composition was added to 2400 parts by weight (dry basis) of a cellulose pulp and the mixture so obtained was employed in the production of the liner ply of a multi-ply paperboard.

In comparison with a customary paperboard with a liner ply with clay/talc filler the following results were obtained:

	Paperboard with clay/talc filler	Paperboard with $CaCO_3$ + 4% latex as filler
Basis weight of board with liner ply in g/m^2	72	60
Basis weight of board without liner ply in g/m^2	61.3	49.2
Basis weight of clay-liner ply in g/m^2	10.7	10.8
Total basis weight in g/m^2	350	350
Ash content of loaded liner ply in %	10.5	24
Total ash content in %	14	17
Moisture content in %	5.6	6.2
Brightness	80.5	82.0
Burst resistance in kg/cm^2	6.7	6.0
Stiffness according to Taber (machine direction)	195	200
Stiffness according to Taber (cross direction)	100	100
Dennison wax test	7	7
Delamination	6.3	6.8

Translator's note: The basis weight descriptions for the paperboard components appear to be in error in the original German text.

It is evident at once that, in spite of a considerable reduction of the weight of the expensive liner ply, the brightness is improved, whereas the mechanical properties remain the same.

Patent Claims

1. Composition for replacement of fibers in a paper-type web material based upon a fine-particled inorganic filler like calcium carbonate, so characterized that the filler is present in the form of particles with cationic potential and is combined with an anionic polymeric resin.

2. Composition according to claim 1, so characterized that it contains calcium carbonate as filler, which is treated with cationic starch.

3. Composition according to claims 1 or 2, so characterized that the resin is so chosen that a film formed from it is inelastic and has an elongation at rupture of 200% maximum, preferably of less than 20%.

4. Composition according to claims 1, 2, or 3, so characterized that the anionic resin is present as an aqueous latex.

5. Composition according to claims 1, 2, 3, or 4, so characterized that the anionic resin is a styrene/butadiene copolymer.

6. Composition according to claims 1 to 5, so characterized that the ionic properties of the filler and of the polymer are equalized, so that the total composition has a zeta potential of essentially 0.

7. Composition according to claim 6, so characterized that the resin particles adhere to the individual filler particles.

8. Composition according to claims 1 to 7, so characterized that it is present as an aqueous dispersion.

9. Process for the production of paper, so characterized that one adds to the pulp for the paper production a mixture of an aqueous latex of an anionic resin and an aqueous dispersion of a particulate cationic inorganic filler, forms the pulp into a wet web, and after dewatering, dries it.

10. Paperboard or similar web material containing fine-particled inorganic fillers, so characterized that an anionic polymeric resin adheres with ionic force to the inorganic filler particles.

Translation December 11, 1981
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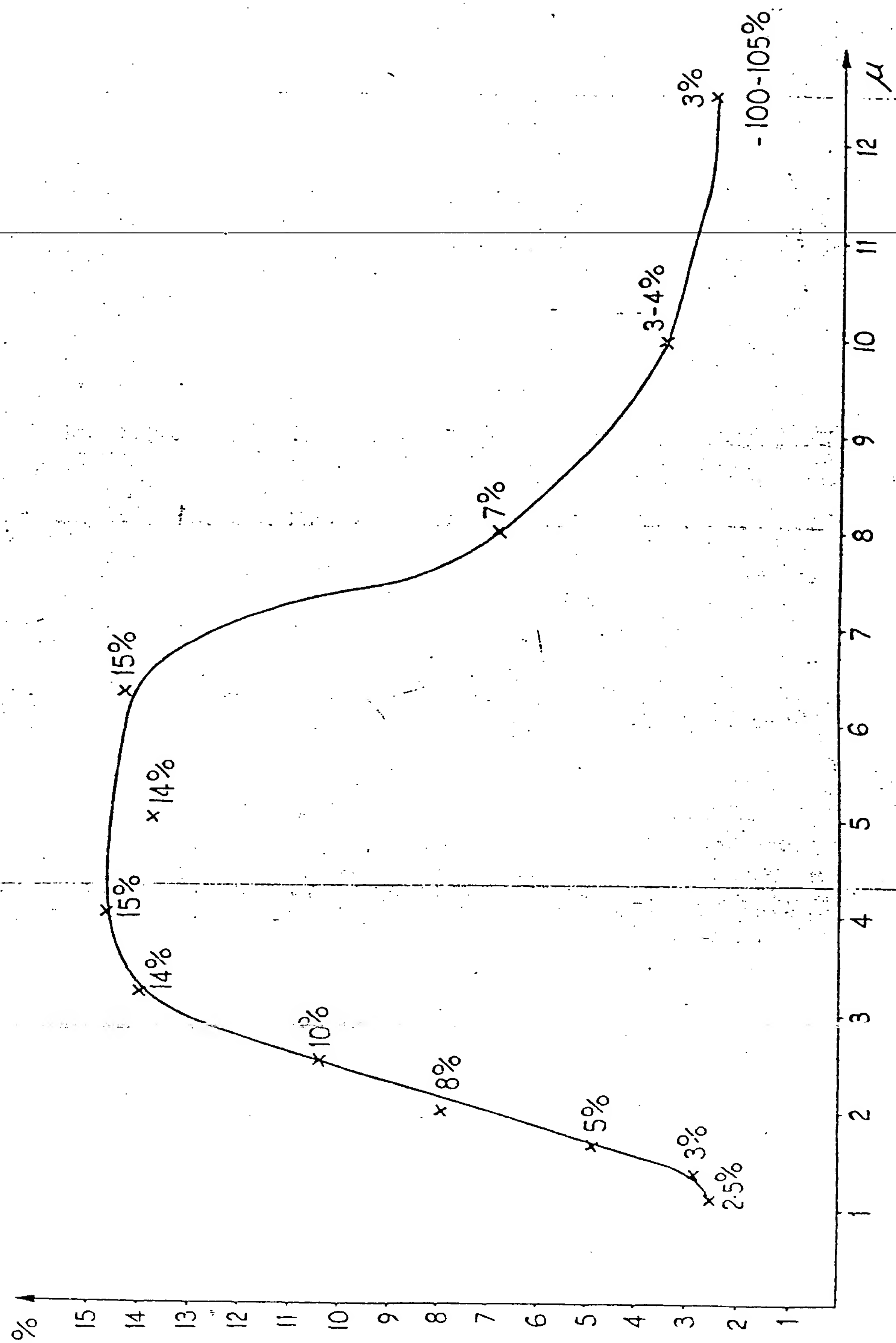
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DEUTSCHES PATENTAMT

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WEST GERMANY
GROUP 173
CLASS 162
RECORDED

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(11) **Offenlegungsschrift 25 16 097**

(21) Aktenzeichen: P 25 16 097.8
(22) Anmeldetag: 12. 4. 75
(43) Offenlegungstag: 6. 11. 75

(30) Unionspriorität:
(32) (33) (31) 19. 4. 74 Großbritannien 17371-74

76051W/46 A97 F09 GRAC 19.04.74
GRACE W R CO *DT 2516-097
19.04.74-GB-017371 (06.11.75) D21h-03/78

Filler for replacement of fibres in paper or board - contg. cationic inorganic filler and anionic resin

A compsn. for replacement of fibres in a sheet of paper or similar material is based on positively charged finely divided inorganic filler (such as $CaCO_3$) particles, which are mixed with an anionic resin so that the resin particles adhere to the surface of the filler particles.

ADVANTAGE

Greater proportions can be used than is possible with conventional fillers without any increase in strength loss, so that improved opacity can be obtd.

DETAILS

The filler can be a commercial cationic prod. or can be made cationic by suitable treatment, e.g. $CaCO_3$ can be mixed with a small amt. of cationic starch in order to impart a positive zeta potential. Other suitable fillers are $CaSiO_4$, talc, clay diatomaceous earth, $CaSO_4$, SiO_2, mixts. of these fillers or a mixt. of $CaSO_4$ and $Ca_3(PO_4)_2$. A suitable cationic grade of $CaCO_3$ is available as Micocell (RTM). The resin is pref. used as an aqueous latex, which on drying at room temp. is not film-forming or gives an inelastic film.

A12-W6.

i.e. one having a max. extensibility < 200% and pref. < 20%. The pref. polymer is a styrene-butadiene copolymer having a styrene content of at least 60 wt.%. Other suitable addition resins are polyvinyl acetate and acrylic copolymers.

PROCESS

The compsns. can be made by mixing an aqueous latex with an aqueous suspension of the finely divided inorganic filler. The latex is pref. added to the suspension in the proportion of 1-20 pts. wt. resin to 100 pts. wt. dry filler. The compsns. can be added in the proportion of 5-50% on cellulose fibres to the pulp suspension. Pulps contg. fillers are partic. suitable for use in surface plies of multi-ply boards, the surface ply pref. comprising 10-12 g/m^2 of board.

EXAMPLE

A typical paper comprises 50 pts. wt. cellulose fibres, up to 48 pts. wt. cationic $CaCO_3$ (contg. 0.6 wt.% cationic starch) and 1-10 pts. wt. polymer.(17 pp.).

Duplicate

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